Contaminants in surface water and sediments around the Tynagh Mine, Galway, Ireland.

O'Neill, A., Phillips, D. H., Bowen, J., & Sen Gupta, B. (2015). Contaminants in surface water and sediments around the Tynagh Mine, Galway, Ireland. *Science of the Total Environment*, *512-513*, 261-272. https://doi.org/10.1016/j.scitotenv.2015.01.026

Published in:
Science of the Total Environment

Document Version:
Peer reviewed version

Contaminants in surface water and sediments near the Tynagh silver mine site, County Galway, Ireland

A. O'Neill[a], D.H. Phillips[a,*], J. Bowen[a], B. Sen Gupta[b]

[a]School of Planning, Architecture and Civil Engineering, Queen's University of Belfast, Belfast, BT9 5AG, Northern Ireland

[b]School of the Built Environment, Heriot Watt University, Edinburgh, Scotland

doi:10.1016/j.scitotenv.2015.01.026

Cite paper as:

O'Neill, A., D.H. Phillips, J. Bowen, and B. Sengupta. 2015. Contaminants in surface water and sediments around the Tynagh Mine, Galway, Ireland. Science of the Total Environment. 512-513: 261-272.

Abstract

A former silver mine in Tynagh, Co. Galway, Ireland is one of the most contaminated mine sites in Europe with maximum concentrations of Zn, As, Pb, Mn, Ni, Cu, and Cd far exceeding guideline values for water and sediment. The aims of this research were to 1) further assess the contamination, particularly metals, in surface water and sediment around the site, and 2) determine if the contamination has increased 10 years after the Environmental Protection Agency Ireland (EPAI) identified off-site contamination. Site pH is alkaline to neutral because $CaCO_3$-rich sediment and rock material buffer the exposed acid generating sulphide-rich ore. When this study was compared to the previous EPAI study conducted 10 years earlier, it appeared that further weathering of exposed surface sediment had increased concentrations of As and other potentially toxic elements. Water samples from the tailings ponds and adjacent Barnacullia Stream had concentrations of Al, Cd, Mn, Zn and Pb above guideline values. Lead and Zn concentrations from the tailings pond sediment were 16 and 5 times higher, respectively, than concentrations reported 10 years earlier. Pb and Zn levels in most sediment samples exceeded the Expert Group (EGS) guidelines of 1000 and 5000 mg/kg, respectively. Arsenic concentrations were as high as 6238 mg/kg in the tailings ponds sediment, which is 62 and 862 times greater than the EGS and Canadian Soil Quality Guidelines (CSQG), respectively. Cadmium, Cu, Fe, Mn, Pb and Zn concentrations in water and sediment were above guideline values downstream of the site. Additionally, Fe, Mn and organic matter (OM) were strongly correlated and correlated to Zn, Pb, As, Cd, Cu and Ni in stream sediment. Therefore, the nearby Barnacullia Stream is also a significant pathway for contaminant transport to downstream areas. Further rehabilitation of the site may decrease the contamination around the area.

1. Introduction

A 1960 soil survey, conducted by Irish Base Metals, uncovered a major reservoir of metalliferous minerals within close proximity to Tynagh village, Co. Galway, Ireland (Environmental Protection Agency Ireland, 2009 and Henry, 2011). By 1961, exploration of the area commenced. Three ore bodies were discovered in the area. Following discovery of the ore bodies, open cast mining began in 1965 until 1974, and underground mining occurred via 84 km of portals (Brogan, 2003 and Environmental Protection Agency Ireland, 2009). The secondary ore body was found in a karst sinkhole and mineralization was formed by primary ore weathering. At the Tynagh Mine, all raw materials were processed on-site which included 9.9 million tonnes of economic grade Pb, Zn, Cu and Ag until 1982 when it closed (EPAI, 2009).

After all mining activities ended, initial remediation work was undertaken to stabilise the site, which included backfilling 71 km of underground portals, and contouring tailings piles (EPAI, 2009). The remediation work was considered inadequate by local residents and council members who raised concerns regarding the potential off-site contamination posed by the abandoned mine (EPAI, 2009). The concerns of the local residents and farmers were not addressed until 2002, when the Tynagh Mines Liaison Group set-up a protocol to 'protect human health, animal health and the environment' in the Tynagh Mine Area (TMA) (Brogan, 2003). To determine whether a contamination issue existed and whether this contamination posed a threat to the receptors, the Environmental Protection Agency Ireland (EPAI) conducted a risk assessment into the presence and extent of mine-sourced metals in surface water, soils, sediments, mining waste and tailings at the TMA in 2003 (Brogan, 2003). Generally, all surface water samples analyzed were below the recommended livestock standard for ingestion of that particular contaminant, thus indicating that there is no unacceptable risk on or around the TMA to grazing livestock. Nevertheless, the investigation also identified high levels of potentially toxic elements in water and sediment samples around the site. Concentrations of anions and a number of metals were greater than the Regulations for the Quality of Surface Water Intended for the Abstraction of Drinking Water (SI No. 294/1989). As a result, the EPAI recommended that all access to the Barnacullia Stream should be restricted to livestock (Brogan, 2003). The aims of this research were to 1) further assess the contamination, particularly metals, in surface water and sediment around the former Tynagh silver mine, Co. Galway, Ireland, and 2) determine if the contamination has increased over time 10 years after the EPAI identified off-site contamination.

2. Materials and methods

2.1. Study area

The TMA is a former silver mine in Tynagh, Co. Galway, west Ireland (Fig. 1), which lies 53° 15′ N, 8° 37′ W. The TMA covers a total of area of 115 ha and lies approximately 8.05 km from Lough Rea town and 20.9 km from Ballinasloe town. At present, the site is partially occupied by 1) Tynagh Energy Limited, 2) Priority Drilling Ltd., and 3) Milchem Equisport Centre. The main features of the

present TMA include 1) two tailings ponds containing dredged mine sediment, 2) a flooded open cast mine, and 3) heaped tailing spoils and solid waste containing remnants of past mining activities. The mine is situated in a sprawling countryside, which is primarily used for cattle pasture and mainly inhabited by farming families (EPAI, 2009).

The TMA lies within the River Shannon Catchment Area, which flows from west to east, draining into the Kilcrow River (Environmental Protection Agency Ireland, 2009 and Henry, 2011). Two streams run parallel to and within the northern and southern boundaries of the TMA, the Barnacullia Stream and the Derryfrench Stream, respectively (Fig. 1). Due to close proximity to the open cast mine and waste, water from these streams is deemed not fit for human or animal consumption (Brogan, 2003). Both streams are bordered by dense hedge vegetation and gates to prevent cattle from gaining access to the water.

The west of Ireland experiences a moist temperate maritime climate, which is directly influenced by the South Westerly prevailing winds of the North Atlantic Current. This moist air mass is responsible for cool summers of a maximum temperature of ~ 16 °C and mild winters with a minimum temperature of ~ 6 °C (Met Office, 2013). The region experiences an average annual precipitation total of ~ 1156 mm. The mine is on a higher elevation compared to areas to the north, and on a lower elevation compared to areas to the south.

2.2. Geology

The TMA is underlain predominantly by Lower Carboniferous Waulsortian Limestone and an Old Red Stone deposit, which are intersected by the deep seated North Tynagh Fault. This fault was a critical factor in the formation of mineral deposits during the Carboniferous period. It also aided in the movement of acidic water that was responsible for the decalcified and weathering of several million tonnes of rock throughout the Tertiary (Henry, 2011). There are eight primary ore mineralisations present within the TMA, which include arsenopyrite (FeAsS), barite ($BaSO_4$), bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$), galena (PbS), pyrite (FeS_2), sphalerite (ZnS) and tennanite (CuO) (Brogan, 2003 and Environmental Protection Agency Ireland, 2009); therefore, the area is naturally high in sulphides (Brogan, 2003).

2.3. Water and sediment sampling

Following a similar plan to the EPAI (2003), the sampling phase in this study included a 1) Control area (background): The Castletown Stream is outside of the TMA catchment area and samples from it were compared to samples collected in other areas of the study; 2) Mine area: These sampling locations are within the northern boundary of the TMA, and include the tailings ponds, and a ditch at the base of the tailings ponds; and 3) Barnacullia Stream: These sites are along and within the Barnacullia Stream, which flows southwest to northeast and is sourced from within the northern boundary of the TMA. From that point, the stream flows east along the northern boundary of the mine

prior to deflecting north-eastwards and flowing for 0.5 km before converging with the Castletown Stream. The water and sediment samples were collected similarly to the methods used by the EPAI in 2003 for accurate comparisons. Water samples were collected in early October starting from the furthest location downstream, and sequentially sampled with movement upstream. Twenty-six surface water samples were collected in glass bottles. Five of the stream samples were from the same locations as in the previous EPAI study (Brogan, 2003) (Fig. 1). The earlier EPAI study concentrated more on the mine spoil area, while our study concentrated more on the stream water and sediments. These sampling points were also geo-referenced with a Garmin GPSMAP 78 (Garmin (Europe) Ltd, Southhampton, England, UK).

For stream water sampling, the bottles were rinsed downstream three times prior to filling (Brogan, 2003 and Buschmann et al., 2007). Duplicate water samples were collected for cation and anion analysis at each sampling point. To preserve the sample for cation analysis, water samples were acidified to a pH of less than 2 with 1% concentrated HNO_3 (Jung, 2001, Signes et al., 2008 and Romero et al., 2010). All samples were kept in cold storage until analyzed (Jung, 2001).

Twenty-one sediment samples were taken after the corresponding surface water samples were collected. A 10-cm length sediment sample was taken from the bed of the stream or tailings pond with an auger (Jung, 2001 and Camm et al., 2004). When the stream bed was impermeable, either a sediment sample from the adjacent submerged banks or a gravel sample from the bed was taken instead. The sample was sealed in a polyethylene bag and kept in cold storage until air drying. After air drying, the sediment samples were ground to pass through a ≤ 0.45 μm sieve.

2.4. Geochemical analysis

The pH of the stream water was measured in-situ at sampling points in the field (Jung, 2001 and Romero et al., 2010) before water and sediment samples were collected. The pH measurements were taken with a hand held waterproof Hanna HI 991301 pH/EC/TDS, temperature meter (Hanna Instrument Ltd, Bedforshire, England, UK). Both water and sediment samples were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) with a PerkinElmer Optima 5300 DV (PerkinElmer, Waltham, MA, USA) using argon as the cell gas for total Ag, Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, S and Zn according to BS 6068–2.60: 1998. Working standards were made from Inorganic Ventures reference standards IV-STOCK-13 with a matrix of 5% HNO_3 (v/v) and IV-ICPMS-71A with a matrix of 3% HNO_3 (v/v) (Inorganic Ventures, Christiansburg, VA, USA). Calibration with reference samples and blanks, and replicate analysis for quality control were carried-out to ensure reliability of analytical data. Recovery obtained and limits of detection (LOD) for the metals analyzed by ICP-OES are in Table S1. The sediment samples underwent microwave digestion in 10 ml of HNO_3 for 15 min, followed by filtering through a 0.45 μm filter prior to ICP-OES analysis. Loss-on-ignition was used to measure OM where samples were heated in a Carbolite RHF 1600 furnace (Carbolite, Derbyshire, England, UK) at 550 °C for 4 h (Heiri et al., 2001).

Anions in the unacidified water and sediment samples were measured by ion chromatography (IC) using a Dionex DX500 system (Thermo Fisher Ireland Ltd, Dublin, Ireland), for fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}). Working standards used in the analysis of these anions were made from Ultra Scientific IC 1000 mg/L reference standards (Ultra Scientific, VWR Ireland, Dublin). Relative standard deviation and other calibration information regarding QA/QC for the IC analysis are shown in Table S2. Deionized water was added to 1 g of sediment at a ratio of 5:1 water:sediment, then shaken on a Jeio Tech SKC-7075 orbital platform shaker (Jeio Tech Co., Ltd (Europe UK), Oxfordshire, England, UK) for 30 min at 240 rpm. The samples were filtered through filter paper with a particle retention size of 5–13 μm using a vacuum pump (Lim et al., 2008).

2.5. Mineralogical analysis

Hydrogen peroxide (H_2O_2) was used to remove OM from mineral grains for better analysis of sediment by X-ray diffraction (XRD). Each sample was washed free of H_2O_2 with deionized water, air dried, finely ground (0.002 to 0.005 mm) using a mortar and pestle (Osán et al., 2002, Camm et al., 2004 and Di Luca et al., 2011), and placed in a packed mount for XRD analysis. XRD analysis of sediment was performed using a PANalytical X'Pert Pro Materials Research Diffractometer (PANalytical, Cambridge, England, UK) with an angular range (3–80 2θ), step size (0.04 2θ) and intensity range (2 counts/s^{-1}). Additionally, selected soil samples were impregnated with a resin, polished, carbon coated and analyzed with a Jeol 6500 FEG (Jeol (UK) Ltd, Herts, England, UK) scanning electron microscope (SEM) equipped with an Oxford Instruments INCAWave spectrometer for energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) (Oxford Instruments Plc, Oxford, England, UK).

2.6. Standard guideline values

Data in this study was compared to the same water and sediment standard guideline values that were used in the previous EPAI study 10 years before (Brogan, 2003) (Table 1). The current study also compared water geochemical parameters to the SI No. 272/2009 guideline values which are currently being used in Ireland in regards to the Water Framework Directive. The SI No. 272/2009 guidelines also include values for Pb, Hg, Cd, and Ni which are on the priority substance list (Directive 2008/105/EC environmental quality standards).

3. Results and discussion

3.1. Sediment and surface water contamination in the Tynagh Mine Area (TMA)

Sediment and surface water samples were collected from the flooded tailings ponds and a ditch lying at the base of abandoned tailings piles for geochemical analysis (Fig. 1 and Fig. 2a–d). Although both tailings pond sediment samples had similar anion concentration trends (Fig. 2b), sediment from

sampling point M8, collected closer to the flooded open cast mine, had a SO_4^{2-} concentration ~ 33% greater than sediment from sampling point M7 which was collected further south, possibly due to being closer to the flooded open cast mine. Sulphate concentrations were also above the SI No 294/1989 guideline value for water (Fig. 2a). The elevated SO_4^{2-} concentrations were greater than the guideline value of 200 mg/L for both water samples. Ditch water at the base of the tailings piles (M9 and M10) had high SO_4^{2-}concentrations. Total S^- is higher than SO_4^{2-} in all of the water and sediment samples because it is a combination of SO_4^{2-} and all of the other sulphur forms (Fig. 2, Fig. 3 and Fig. 4). Water collected from sampling point M11 also contained NO_3^- (663 mg/L) which exceeded the SI No 294/1989 guideline value possibly due to contamination from adjacent agricultural fields. Additionally, water from sampling points M8, M9 and M11 had F^- concentrations above the SI No 272/2009 guideline value.

Similar to the pH (8.03) values reported by the EPAI 2003, in-situ pH measurements showed that the tailing ponds were more alkaline than the upper Barnacullia Stream (7.85 to 6.21) (Fig. 2a). The tailings ponds; however, had a much lower Ca content, indicating an influence by the ore minerals and not the limestone host rock. Similarly, Navarro et al. (2008) reported neutral to alkaline environments within an abandoned mining area in SE Spain that were associated with carbonates. Water from sampling points M9 and M10 from the ditch were the only samples in the TMA to have a Ca concentration greater than the WHO drinking water standard value (Fig. 2c). These findings suggested that the ditch water may be fed from another source such as a spring flowing through limestone bedrock sourced from beneath the tailings piles.

Similar to a study by Romero et al. (2010), XRD detected quartz, calcite, dolomite, barite and pyrite. Additionally, SEM analysis identified barite and arsenopyrite in sediment from the mine tailings pond, which confirmed elevated concentrations of As, Ba, Fe and S in sediment. The minerals present within the tailings ponds were expected to be oxidised forms of those present in the ore bodies, due to their exposure to the environment during and after mining activity. In the EPAI (2003) study, As averaged 332 mg/kg within the tailings pond sediment; however, it was below WHO drinking water limits and SI 272/2009 guideline values in the surface water collected from the TMA. A notably higher As sediment concentration was also observed for the tailings ponds, with a maximum of 6238 As mg/kg, which is 62 and 862 times greater than the EGS and CSQG guideline values, respectively (Fig. 2d). Additionally, a sediment sample from the ditch (M9) exceeded the EGS guideline value. This also agrees with Camm et al. (2004) who observed As tailings concentrations exceeding 100 mg/kg at a former mine in south England.

Arsenic, Cd, Cu, Hg, Mn, Ni, Pb and Zn exceeded the CSQG guideline values in sediment samples collected from all of the mine tailings ponds and ditch sampling points. Chromium and Ag CSQS values were also exceeded in sediment collected from sampling points M7 and M8, respectively. Except for Ag and Ba, greater concentrations of As and metals were found in sediment from sampling point M7, compared to sediment from sampling point M8 (Fig. 2d). The EPAI generally observed

lower concentrations of metals in tailings pond sediment than that found in this study. For example, the concentrations of Pb and Zn observed in 2003 were 16 and 5 times less than those observed in 2013, respectively. Even though the sediments from the TMA were high in metals, many of these metals were below LOD by ICP-OES (Table S1) in the surface water from the TMA. Concentrations of Ag, Hg, As in all water samples collected from the TMA and the Castletown Stream control points were below LOD, while concentrations of Pb, Cu, Cr, Cd, were below LOD in water collected from sampling points M10, M11 and from the Castletown Stream. Aluminium was below LOD in water from sampling points M10 and M11, while Ni was below LOD in water from sampling point M11. Nevertheless, it is noteworthy that the SI No 294/1989 and SI No 272/2009 guideline values for Cd, and the SI No 272/2009 guideline value for Hg are lower than the ICP-OES LOD measurements (Table S1), which does not allow comparison with the guideline values for Cd and Hg that were used in this study.

Sediment samples from the tailings ponds and ditch (M7, M8 and M9) also had concentrations of Cd, Ni, Cu, Hg, Pb, Zn and Mn above CSQG guideline values (Fig. 2c) and elevated Ca, Al and Fe concentrations. SEM-EDS and WDS analysis show high concentrations of contaminants, mainly metals, in mine tailing sediments. Lead, As and Zn were as high as 63.2%, 9.4%, and 16.12%, respectively (Fig. 5a,b). Also, coatings containing Pb and to a lesser extent Zn, were observed on silicate minerals from tailing sediment (M8) (Fig. 6) indicating that metals were released and subsequently sorbed onto mineral surfaces at the site. The presence of Zn and Pb, which are associated with sphalerite and galena, respectively, is characteristic of Ag mines (Jung, 2001). However, concentrations Pb and Zn as well as Cd and Cu, in this study were orders of magnitude greater than that observed by Jung (2001). The concentrations of Pb and Zn from the tailings pond sediment reported by the EPAI (2003) were 16 and 5 times less, respectively, than in this study. Most sediment samples from the tailings ponds and ditch at the bottom of the northern tailings pile had As, Pb and Zn concentrations that exceeded the EGS guidelines of 100, 1000 and 5000 mg/kg, respectively (Fig. 2d), while corresponding water samples had Pb and Zn concentrations at or exceeding abstraction guidelines from sampling points M7, M8 and M9. Additionally, the southernmost tailing pond water sample (M8) also had higher concentrations of Zn, Pb and other metals compared to water from sampling point M7. This trend was not reported by the EPAI (2003), suggesting that processes over the past decade, such as weathering, have exposed and mobilised metals. These findings were supported by other studies that report high levels of metals within abandoned mine tailings (Lim et al., 2008, Romero et al., 2010, Qiao et al., 2011 and Zornoza et al., 2011).

3.2. Sediment and surface water contamination in the Barnacullia Stream

Anions measured in surface water samples collected from the Barnacullia Stream and Castletown Stream (control) were below the SI No 294/1989 guidelines (Fig. 3a; Table 1 and Table 2). However,

F^- was above the SI No 272/2009 guideline value in water from sampling point D9. These values are also similar, but less than those reported by the EPAI in 2003 (Brogan, 2003 and Environmental Protection Agency, 2003). The order of abundance of anions in the Barnacullia Stream water was SO_4^{2-} followed by Cl^-, NO_3^-, F^- and PO_4^{3-}, with a similar order of abundance for sediment anions (Fig. 4a).

The pH of the upper Barnacullia Stream water (7.85 to 6.21) (Fig. 3a) was less alkaline than the tailing ponds. Similar to the EPAI 2003 pH (8.03) values, stream water pH decreased within increasing proximity to the TMA perhaps due to weathering of sulphide minerals within the TMA (Navarro et al., 2008). This theory is supported by the increasing SO_4^{2-} content with increasing proximity to the mine. For example, values of SO_4^{2-} between sampling points D5 and D13 were much greater than SO_4^{2-} values downstream, with an average concentration of 146 mg/L, though the guideline value was not exceeded (Fig. 3a). Generally, in the upper Barnacullia Stream most sediment samples had a high total S^- and SO_4^{2-}concentrations that exceeded the corresponding water sample, with the exception of sediment from sampling points M1 and M4. Water samples from the upper Barnacullia Stream had an average SO_4^{2-}concentration of 163 mg/L, which is below the guideline value used in this study. Sediment from sample point M5 had a significantly greater SO_4^{2-} content compared to concentrations downstream. Average SO_4^{2-} content recorded during this study was less than that observed by the EPAI, suggesting that the mobilisation of SO_4^{2-} from local ore bodies which contain sulphide bearing minerals, has decreased over the past decade. This difference may have been due to a seasonal variation as the EPAI collected samples in June and the samples for the current study were collected in October. As SO_4^{2-} content of water samples from the Castletown Stream was much lower than that reported by the EPAI for the same location (Brogan, 2003), it can be deduced that the catchment areas outside of the TMA are influenced by the local limestone geology. Anion concentrations clearly decreased at the confluence point, due to dilution by the Castletown Stream (Fig. 3a). Nevertheless, SO_4^{2-} and total S^- concentrations were greater in water sampled downstream of the confluence point. In-situ pH analysis of the water showed that downstream of the Castletown Stream is more alkaline than upstream, as a pH of 7.30 and 6.98 were observed, respectively. The EPAI recorded a pH of 7.70 for the water at a similar location (Brogan, 2003).

Additionally, NO_3^- and PO_4^{2-} concentrations in sediment samples M4 and M5, near the source of the upper Barnacullia Stream, were greater than corresponding water samples. These higher NO_3^- and PO_4^{2-}concentrations in the sediment samples compared to the corresponding water samples may be due to the leaching of fertilizers from the adjacent fields which adsorbed onto the OM in the stream sediment. The sediment sample collected downstream of the confluence point (D1), contained 60.2 and 4.33 mg/kg of NO_3^- and PO_4^{2-}, respectively, which generally decreased upstream. Sediment from sampling point D8, located upstream of sampling point D1, also had higher than average NO_3^- and PO_4^{2-} contents.

XRD detected quartz, calcite, dolomite, barite, and pyrite in sediment samples collected from the upper Barnacullia Stream, which is characteristic of the Lower Carboniferous Waulsortian Limestone geology underlying the Shannon Catchment Area (Clifford et al., 1986). All sediment samples from the Barnacullia and Castletown Streams had very high Ca concentrations, > 100,000 mg/kg, which agreed with the Ca concentration in stream water samples and is characteristic of a limestone environment (Table 2). Additionally, Ca content in sediments increased downstream, suggesting the limestone bedrock acts as a natural buffer against acidic conditions created by elevated oxidation of sulphide minerals. The water from sampling point M5, at the most western point of the northern boundary of the mine site, had an Al concentration eleven times higher than the SI No. 294/1989 guideline value. Nevertheless, water from sampling points M1 to M4 also had higher Ca contents than in water from sampling point M5, which may buffer Al (Berger et al., 2000 and Andrews et al., 2003). The water samples collected along the Castletown Stream had a mean Ca concentration of 215 mg/L (Table 2). Weddellite was also detected by XRD and has been reported associated with a high OM content (Griffin et al., 1984 and Clifford et al., 1986), such as that observed along the Barnacullia Stream.

Along the upper Barnacullia Stream within the TMA boundary, concentrations of As, Cd, Cu, Mn, Ni, Pb, Hg, and Zn in sediment exceeded guideline values, while concentrations of Ag exceeded the guideline values in sediment from sampling points M4 and M2 in the stream. Concentrations of As, Cd, Cu and Pb in the sediment sample collected at sampling point M2 were all similar or less than that observed at the same location by the EPAI in 2003; 132 vs 332 mg/kg, 36.5 vs 41 mg/kg, 251 vs 255 mg/kg and 1759 vs 2869 mg/kg, respectively. However, the concentration of Zn in the stream sediment, was significantly greater than that observed by the EPAI; 8590 vs 5162 mg/kg, respectively. Similar to the metal concentrations in water collected on the TMA, several metals and As were below LOD in the water samples taken from the upper Barnacullia Stream. Water concentrations of Ag, Hg and As were below LOD at sampling points M1 to M6. Also, water concentrations of Al and Cr were below LOD, except at sampling points M5, and M4 and M5, respectively. Nevertheless, water concentrations of Cd, Ni, Mn and Zn along sampling points M1 to M6 (Fig. 3a, Table 1) exceeded the SI No 294/1989 guideline values, while Ni also exceeded the SI No 272/2009 guideline value. Lead exceeded the SI No 294/1989 guideline value in water from sampling points M1 to M3 and M6 and also exceeded the SI No 272/2009 guideline value at sampling point M4. Water samples (M1 to M4) collected downstream of sampling point M5 had Fe contents greater than SI No 294/1989 guideline value. According to Navarro et al. (2008), Pb, Zn and Cd along this water body may have originated from sulphide minerals. In the Castletown Stream (control), concentrations of most of the metals in water were below the guideline values used in the study (Fig. 3b; Table 1 and Table 2) for sediment; however, concentrations of Cd, Mn, Hg and Zn in sediments exceeded CSQG guideline values. Sediment As, Pb and Cu concentrations exceeded the CSQG guideline values at all sites along the lower Barnacullia Stream, except at sampling point D3. Arsenic, Pb and Zn concentrations exceeded the EGS guideline values in sediment collected at sampling points D11 and D13, while Pb exceeded the EGS guideline value at sampling points D7 and D8. Zinc concentrations also exceeded the EGS

guideline value in sediment from sampling points D5 and D2 along the Barnacullia Stream. Additionally, Ag concentrations were above the CSQG value in sediment from sampling points D13, D11 and D7. Similarly, the 2003 risk assessment conducted by the EPAI observed elevated levels of Cd, Zn, and also a Pb concentration in sediment exceeding the CSQG guideline value of 30.2 mg/kg in the Castletown Stream. The water from the Castletown Stream (Table 2) had an elevated concentration of Fe, which coincided with the sediment concentration of 6755 Fe mg/kg. Comparatively, this Fe value was significantly less than that observed within the TMA and downstream of the mine. The results of both studies suggested that there is a presence of metals, including As, outside of the TMA. A source of metals contamination was not identified. The metal profile was considered representative of the local geochemical background of the area, as reported byNavarro et al. (2008).

High amounts of metals, including As, also occur in groundwater near the site. Henry (2011) reported that Fe, Mn, Zn, Cu, Ba, Ni and As exceeded the Guideline Threshold Values (GTV) for Europe and the Irish Interim Guide Values (IGV) for ground water in a shallow well 2 m from the TMA boundary and in deep (100 m) wells several km east from the TMA. High concentrations of contaminants in groundwater from the deep wells are thought to be due to flooding of the 34 km of underground mine shafts which has released the contaminants from the Tynagh Fault, while the groundwater in a shallow well near the mine boundary is thought to be contaminated by surface runoff from the mine (Henry, 2011).

Generally, there was a trend of decreasing metal content with increasing distance from the mine area (Fig. 3b) which is a common characteristic of a site where contaminant transport is driven by local climate and hydrology (Jung, 2001, Lim et al., 2008, Navarro et al., 2008, Romero et al., 2010, Hajalilou et al., 2011, Chakraborti et al., 2013, Antunes and Albuquerque, 2013 and Silva et al., 2013). Metal distribution is dependent upon the form of the contaminant. It can either enter into solution, resulting in the contamination of a water body, or adsorb and precipitate onto sediment particles, resulting in sediment contamination (Navarro et al., 2008). Sediment collected from sampling points D13 to D11, located directly after the culvert, had peak concentrations of Ag, As, Cd, Cu, Fe, Mn, Pb and Zn (Table 2; Fig. 4b). Additionally, water samples from the lower Barnacullia Stream were higher in metals compared to water samples from the Castletown Stream (control), which suggests transport of contaminants along the stream from the TMA (Fig. 3b). Concentrations of Ag, Ba, and Mg in all water samples were below the respective guideline values (Fig. 3b); however, the SI No 272/2009 guideline value was exceeded for Cr concentrations in water from sampling points D8 to D6. Also, the SI No 294/1989 guideline value was exceeded for Al concentrations in water from sampling points D4 to D3, Pb concentrations in water from sampling points D9 to D8, and Cu concentrations in water from sampling point D11. Iron concentrations were above the SI No 294/1989 value in water from sampling points D13 and D11 to D9. It is noteworthy that Cd, Cu, Fe, Mn, Pb and Zn concentrations in water were higher than guideline values at one or more locations along the stream from sampling points D5 to D13. With exception of Mn, there were negligible concentrations of

the aforementioned metals within the Castletown Stream, which suggests that the metals were a result of contamination.

These high concentrations of metals and As in the sediments were also confirmed by SEM analysis which indicated a substantial presence of As, Fe, Pb and Zn in sediment collected at sampling point D13. Metals, especially Zn, were detected in coatings on calcite fragments (D13) (Fig. 5c). Barite fragments and colloidal-sized particles high in metals (i.e., lead carbonate precipitates) were examined by SEM analysis in fine sediment from the lower Barnacullia Stream (Fig. 5d) collected immediately after the culvert (D13). Although As concentrations in sediments decreased with distance downstream, SEM detected arsenopyrite in sediment from the Barnacullia Stream.

Sediment metal content decreased significantly at the confluence point between the Barnacullia and Castletown Streams (Fig. 3b) from sampling points D4 and D3, due to dilution by the Castletown Stream and also due to the natural attenuation of the metals, as previously observed by Romero et al. (2010). Nevertheless, downstream of the confluence point higher concentrations of the majority of metals were observed in sediment from sampling point D2, compared to sediment from sampling points D4 and D3. For example, Zn content in sediment from sampling point D2 was approximately three times the EPAI EGS guideline values, whereas the sediment collected at sampling points D4 and D3 contained only 3% of that guideline value. Copper was also higher in sediment collected at sampling point D2, compared to sediment from sampling points D4 and D3. This may be due to legacy contamination where contaminated material was washed from the mine site when it was in operation. Water from both confluence point sampling locations had Al concentrations greater than guideline values. These levels of Al in the water did not occur upstream of the Barnacullia Stream, but were observed within the Castletown Stream. Water from the confluence point (D3) and downstream of the convergence (D1) also had Mn concentrations that exceeded the SI No 294/1989 guideline value of 0.05 mg/L. With the exception of Mn, water samples collected from sampling point D1 did not exceed any other guideline value in lower Barnacullia Stream water. Similar Mn concentrations were observed for the Castletown Stream control area and along the lower Barnacullia Stream. The EPAI analysis of the convergence area showed a similar geochemical profile to that observed in the sediment from sampling point D2. Concentrations of As (47.7 mg/kg), Cd (21.5 mg/kg), Cu (40.4 mg/kg), Pb (87.5 mg/kg) and Zn (1404 mg/kg) in stream sediment were found to be greater than CSQS guideline values just downstream of the confluence point. The 2003 EPAI study observed similar concentrations of Cd (19 mg/kg), Cu (42 mg/kg) and Zn (1376 mg/kg), but a lower concentration of As (14 mg/kg), and a higher concentration of Pb (277 mg/kg). This indicated that the supply of metals from the TMA has increased over the past decade. Similar findings have been noted by Romero et al. (2010), who found a historic mine in western Cuba to be a significant source of metals despite being inactive for 15 years.

3.2.1. Correlation between contaminants and Fe, Mn and OM in sediment in the Barnacullia Stream

Iron and Mn showed good correlation, and were both highly correlated with Zn, Pb, As, Cd, Cu and Ni in stream sediment (Table 3); however, Fe was better correlated with these metals and As compared to Mn. Arsenic was retained in areas of high Fe-oxide content due to an affinity for Fe-oxides (Patinha et al., 2004,Sarkar et al., 2005, Qi and Donahoe, 2008 and García-Sánchez et al., 2010). Iron and As also were reported to be strongly correlated in groundwater near the TMA (Henry, 2011). Sediment samples high in OM that were comprised mainly of peat from the submerged stream embankments were notably higher in As and metals due to adsorption onto the OM because of its high surface area (Lin and Chen, 1998 and Weng et al., 2001). Additionally, metals were highly correlated with OM (Table 3). SEM analysis revealed OM (peat) encrusted with Zn, Pb, S, Fe, Ca, Si and Al (Fig. 7), and metals in coatings on carbonate minerals in sediment collected from the submerged stream banks (Fig. 5c). Although some metals sorbed onto OM particles were below detection by SEM, Cr, Cd, As, Mn, Ni, and Cu, along with the Pb and Zn, were highly correlated with OM (Table 3). Generally, As and metal concentrations decreased downstream, suggesting that the source of contamination came from the source of the stream. The Barnacullia Stream is thought to be sourced from a spring originating from beneath the tailings ponds area.Brogan (2003) reported that the tailings pond area within the TMA was not adequately lined potentially providing the source of contaminants to the stream.

4. Conclusions

High concentrations of contaminants were observed in water and sediment samples collected within the TMA. In particular, the tailings pond area had levels of Ag, Al, As, Ca, Cd, Cu, Fe, Mn, Ni, Pb and Zn that exceeded guideline values. Also, metal concentrations have increased over the past decade compared to a 2003 EPAI assessment, suggesting that persistent weathering and erosion has released the metal contaminants from ore minerals. Although the site has high levels of sulphide-rich ore, the site pH is alkaline to neutral because the $CaCO_3$-rich geological material acts as a buffer preventing the production of acid mine water. Concentrations Ag, Al, As, Cd, Fe, Mn, Pb and Zn exceeding guideline values were observed in stream water and sediment along the upper Barnacullia Stream, indicating that this water body is a significant pathway of contaminant transport to downstream areas. Iron, Mn and OM were highly correlated and correlated to Zn, Pb, As, Cd, Cu and Ni in stream sediment. Convergence of the Barnacullia and Castletown Streams diluted anions and metals in stream water to below guideline values; however, metal content of stream sediment remained high downstream of the confluence point. Contamination around the site may be decreased dramatically by further rehabilitation of the site. The samples collected were spot samples and were used to compare the results of an EPAI survey carried-out 10 years prior. A more detailed study examining the hydrology and geochemistry of the streams over an extended period of time would be useful in understanding of the dynamics of the streams in the transportation the contaminants away from the site.

References

Andrews, J.E., Brimblecombe, P., Jickells, T.D., Liss, P.S., and Reid, B., 2003. *An Introduction to Environmental Chemistry*, Wiley-Blackwell.

Antunes, I.M.H.R., and Albuquerque, M.T.D., 2013. Using indicator kriging for the evaluation of arsenic potential contamination in an abandoned mining area (Portugal). Sci. Total Environ. 442, 545–52.

Berger, A.C., Bethke, C.M., and Krumhansl, J.L., 2000. A process model of natural attenuation in drainage from a historic mining district. Appl. Geochem. 15, 655–666.

British Standard. 1998. Water quality-determination of 33 elements by inductively coupled plasma atomic emission spectroscopy. BS EN ISO 11885: 1998 BS 6068-2.60:1998. BSI 389 Chiswick High Road, London, Pp 12.

Brogan, J., 2003. Report of the investigation into the presence of lead and other heavy metals in the Tynagh Mines Area, County Galway. Office of Environmental Enforcement, Environmental Protection Agency, Dublin.

Buschmann, J., Berg, M., Stengel, C., and Sampson, M.C., 2007. Arsenic and manganese contamination of drinking water resources in Cambodia: coincidence of risk areas with low relief topography. Environ. Sci. Technol. 41(7), 2146–52.

Camm, G.S., Glass, H.J., Bryce, D.W., and Butcher, A.R., 2004. Characterisation of a mining-related arsenic-contaminated site, Cornwall, UK. J. Geochem. Explo., 82(1-3), 1–15.

Chakraborti, D., Rahman, M.M., Murill, M., Das, R., Siddayya, A., Patil, S.G., Sarkar, A., Dadapeer, H.J., Yendigeri, S., Ahmed, R., and Das, K.K., 2013. Environmental arsenic contamination and its health effects in a historic gold mining area of the Mangalur greenstone belt of Northeastern Karnataka, India. J. Haz. Mat. 262, 1048-1055.

Clifford, J.A., Ryan, P., and Kucha, H., 1986. A review of the geological setting of the Tynagh orebody, Co.Galway. In C. Andrew et al., eds. *Geology and Genesis of Mineral Deposits in Ireland*. Dublin, pp. 419-439.

Di Luca, G.A., Maine, M.A., Mufarrege, M.M., Hadad, H.R., Sánchez, G.C. and Bonetto, C.A., 2011. Metal retention and distribution in the sediment of a constructed wetland for industrial wastewater treatment. Ecolog. Engineer. 37(9), 1267–1275.

Directive 2008/105/EC on Environmental Quality Standards. The European Parliament and of the Council. Priority Substances under the Water Framework Directive.

Environmental Protection Agency, 2003. Towards Setting Guideline Values For The Protection Of Groundwater In Ireland: Interim Report. Environmental Protection Agency, Dublin

Environmental Protection Agency Ireland, 2009. *Historic Mine Sites- Inventory and Risk Classification: Volume I*.

García-Sánchez, A., Alonso-Rojo, P., and Santos-Francés, F., 2010. Distribution and mobility of arsenic in soils of a mining area (Western Spain). Sci. Total Environ. 408(19), 4194–201.

Griffin, G.M., Sawyer, R.K., and Melkote, S.R., 1984. Weddellite Occurrence in Peats and Other Organic Rich Sediments of Florida. J. Sediment. Res. 54(3), 861–868.

Hajalilou, B., Mosafenil, M., Khaleghi, F., Jadidi, S., Vosugn, B., and Fatehifar, E., 2011. Effects of abandoned arsenic mine on water resources pollution in north west of Iran. Health Promot. Perspect. 1(1), 62–70.

Heiri, O., Lotter, A.F., and Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. J. Paleolim. 25, 101–110.

Henry, T., 2011. Tynagh mine groundwater issues. Pp. 587-592. In Rude, Freund and Wolkersdorfer. Mine Water-Managing the Challenges. IMWA 2011.

Jung, M.C., 2001. Heavy metal and trace element contamination of soils and waters in and around the Imcheon Au-Ag mine, Korea. Appl. Geochem. 16, 1369-1376.

Lim, H., Lee, J., Chon, H., and Sager, M. 2008. Heavy metal and trace element contamination and health risk assessment in the vicinity of abandoned Songcheon Au-Ag mine in Korea, J. Geochem. Explo. (96), 223-230.

Lin, J.-G., and Chen, S.-Y. 1998. The relationship between adsorption of heavy metal and organicmatter in river sediments. Environ. Int. 24, 345–352.

Met Office, 2013. Regional Climate: Northern Ireland. Available at: http://www.metoffice.gov.uk/climate/uk/ni/ [Accessed February 20, 2013].

Navarro, M.C., Pérez-Sirvent, C., Martínez-Sánchez, M.J., Vidal, J., Tavar, P.J., and Bech, J., 2008. Abandoned mine sites as a source of contamination by heavy metals-A case study in a semi-arid zone. J. Geochem. Explo. 96(2-3), 183–193.

Osán, J., Kurunczi, S., Török, S., and Van Grieken, S.. 2002. X-Ray analysis of riverbank sediment of the Tisza (Hungary): identification of particles from a mine pollution event. Spectrochimica Acta Part B: Atomic Spectro. 57(3), 413–422.

Patinha, C., Ferreira da Silva, E., and Cardoso Fonseca, E., 2004. Mobilisation of arsenic at the Talhadas old mining area—Central Portugal. J. Geochem. Explo. 84(3), 167–180.

Qi, Y. and Donahoe, R.J.. 2008. The environmental fate of arsenic in surface soil contaminated by historical herbicide application. Sci. Total Environ. 405(1-3), 246–54.

Qiao, M., Cai, C., Huang, Y., Liu, Y., Lin, A., and Zheng, Y., 2011. Characterization of soil heavy metal and trace element contamination and potential health risk in metropolitan region of northern China. Environ. Monitor. Assess. 172(1-4), 353–65.

Romero, F.M., Prol-Ledesma, R.M., Canet, C., Alvares, L.N., and Pérez-Vázquez, R., 2010. Acid drainage at the inactive Santa Lucia mine, western Cuba: Natural attenuation of arsenic, barium and lead, and geochemical behavior of rare earth elements. Appl. Geochem. 25(5), 716–727.

Sarkar, D., Datta, R., and Sharma, S., 2005. Fate and bioavailability of arsenic in organo-arsenical Pesticide applied soils. Part-I: incubation study. *Chemosphere*, 60(2), 188–95.

Signes, A., Mitra, K., Burló, F., and Carbonell-Barrachina, A.A., 2008. Effect of cooking method and rice type on arsenic concentration in cooked rice and the estimation of arsenic dietary intake in a rural village in West Bengal, India. *Food additives & contaminants. Part A, Chemistry, analysis, control, exposure & risk assessment*, 25(11), 1345–52.

Silva, L.F.O., Fdez-Ortiz de Vallejuelo, S., Martinéz-Arkarzo, I., Castro, K., Oliviera, M.L.S., Sampai,C.H., de Brum, I.A.S., de Leão, F.B., Taffarel, S.R., and Madariago, J.M., 2013. Study of environmental pollution and mineralogical characterization of sediment rivers from Brazilian coal mining acid drainage.Sci. Total Environ. 447, 169–78.

Turpeinen, R., Pantsar-Kallio, M., Haggblom, M., and Kairesalo, T., 1999. Influence of microbes on the mobilization, toxicity and biomethylation of arsenic in soil. Sci. Total Environ. 236, 173–80.

Department for Environment Food and Rural Affairs. 2014. Water Framework Directive implementation in England and Wales: new and updated standards to protect the water environment. Crown Publishing Group. pp. 41.

Weng, L. , Temminghoff, E.J.M. , and Van Riemsdijk, W.H. 2001. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. Environ. Sci. Technol. 35, 4436–4443.

Zornoza, R., Carmana, D.M. Acosta, J.A., Martínez-Martínez, S., Weiss, N., and Faz, A., 2011. The Effect of Former Mining Activities on Contamination Dynamics in Sediments, Surface Water and Vegetation in El Avenque Stream, SE Spain. Water, Air, Soil Pollut. 223(2), 519–532.

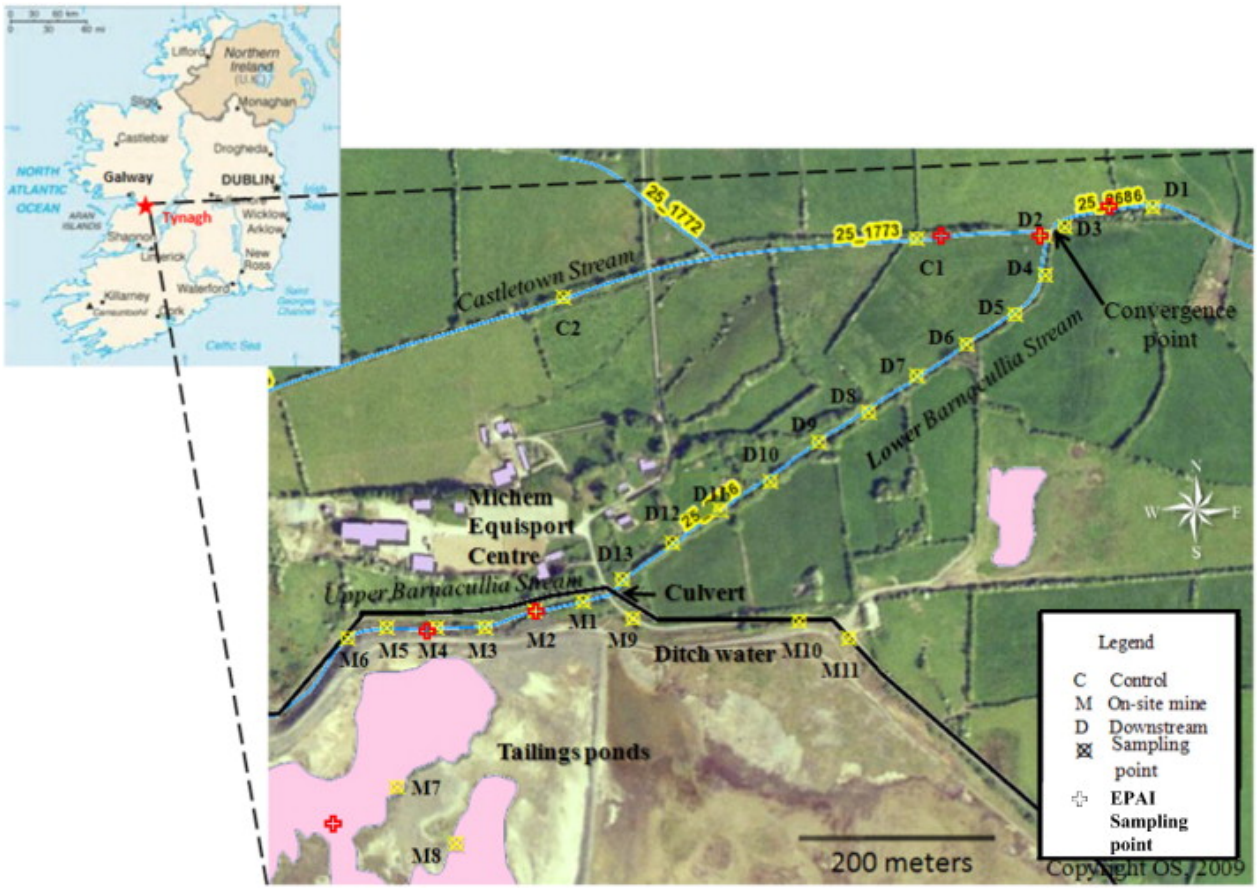


Fig. 1 Location of the sampling points at the study site in Ireland.

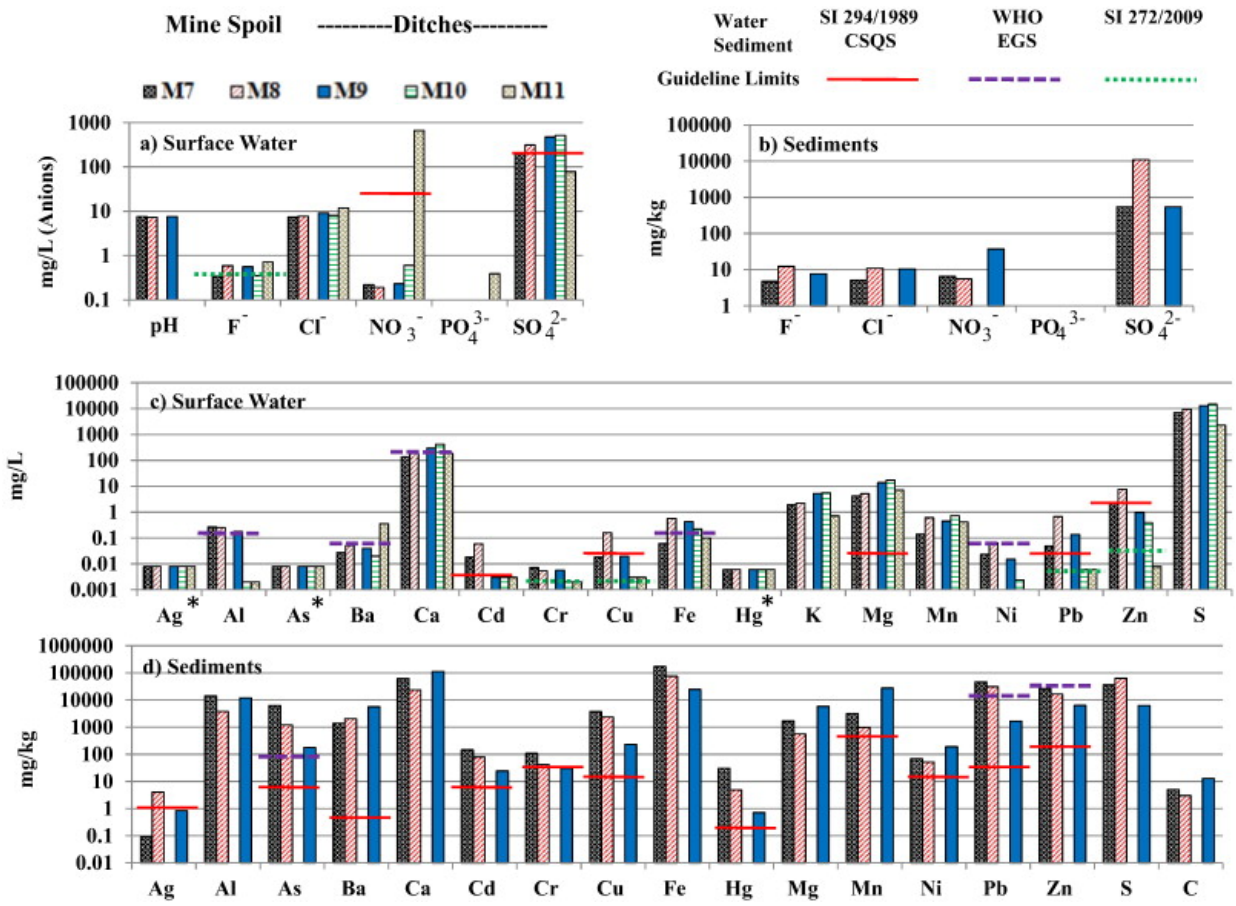


Fig. 2 Comparison of mine spoil and ditch samples showing pH and anions in (a) surface water and (b) sediments, and metals in (c) surface water and (d) sediments. Note: lines across bars indicate limit exceedance. *Below limit of detection.

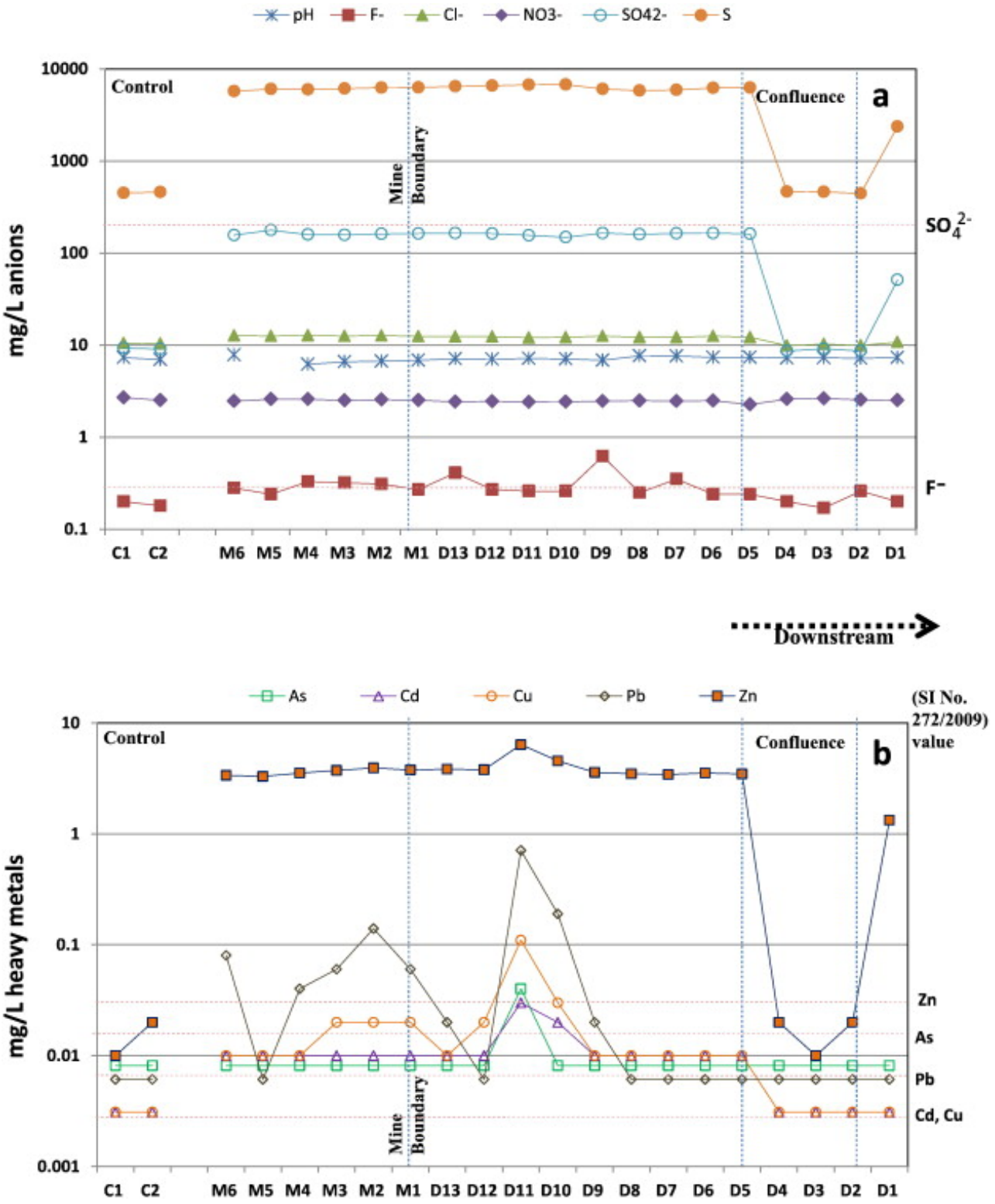


Fig. 3 Surface water a) pH and anions and b) metals from the control (Castletown Stream) and Barnacullia Stream. Note: dotted lines indicate guideline limits.

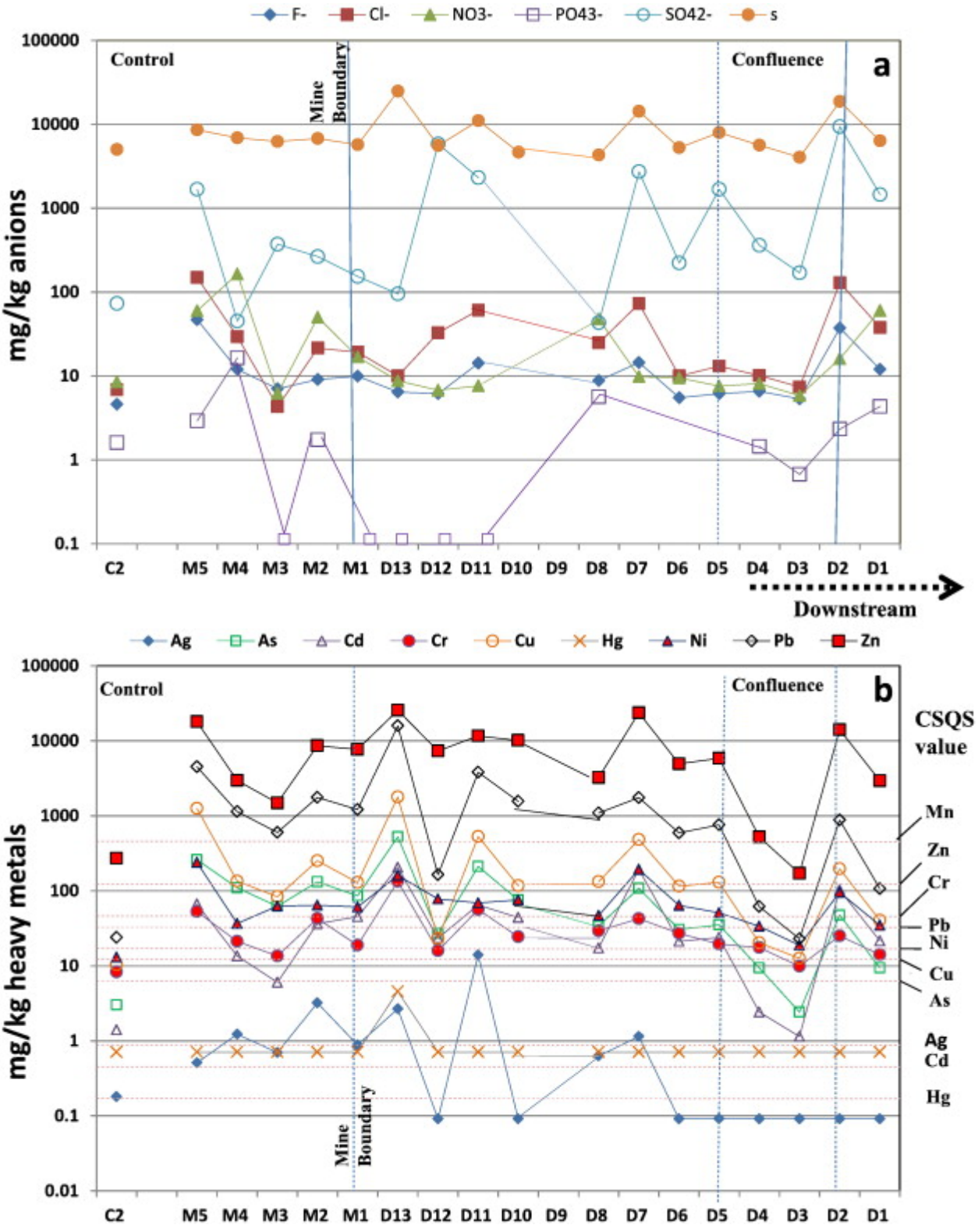


Fig. 4 Sediment a) anions and b) metals from the control (Castletown Stream) and Barnacullia Stream. Note: dotted lines indicate guideline limits.

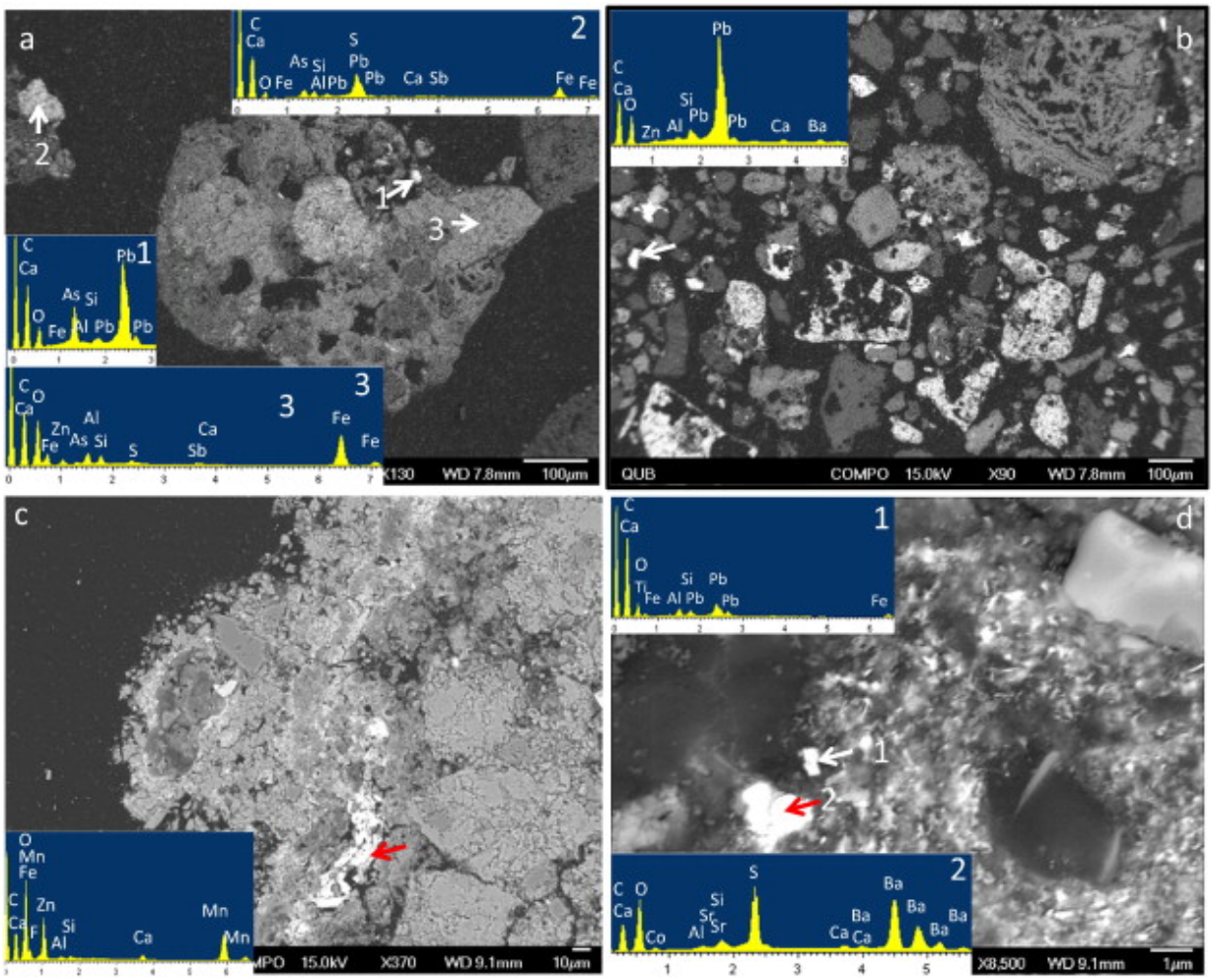


Fig. 5 Photomicrographs of selected samples from TMA mine spoil area sediment showing particles that are high in metals (a, b), and the lower Barnacullia Stream where Zn is associated with Mn-rich coatings on dolomite fragments (c), and fine colloidal-size...

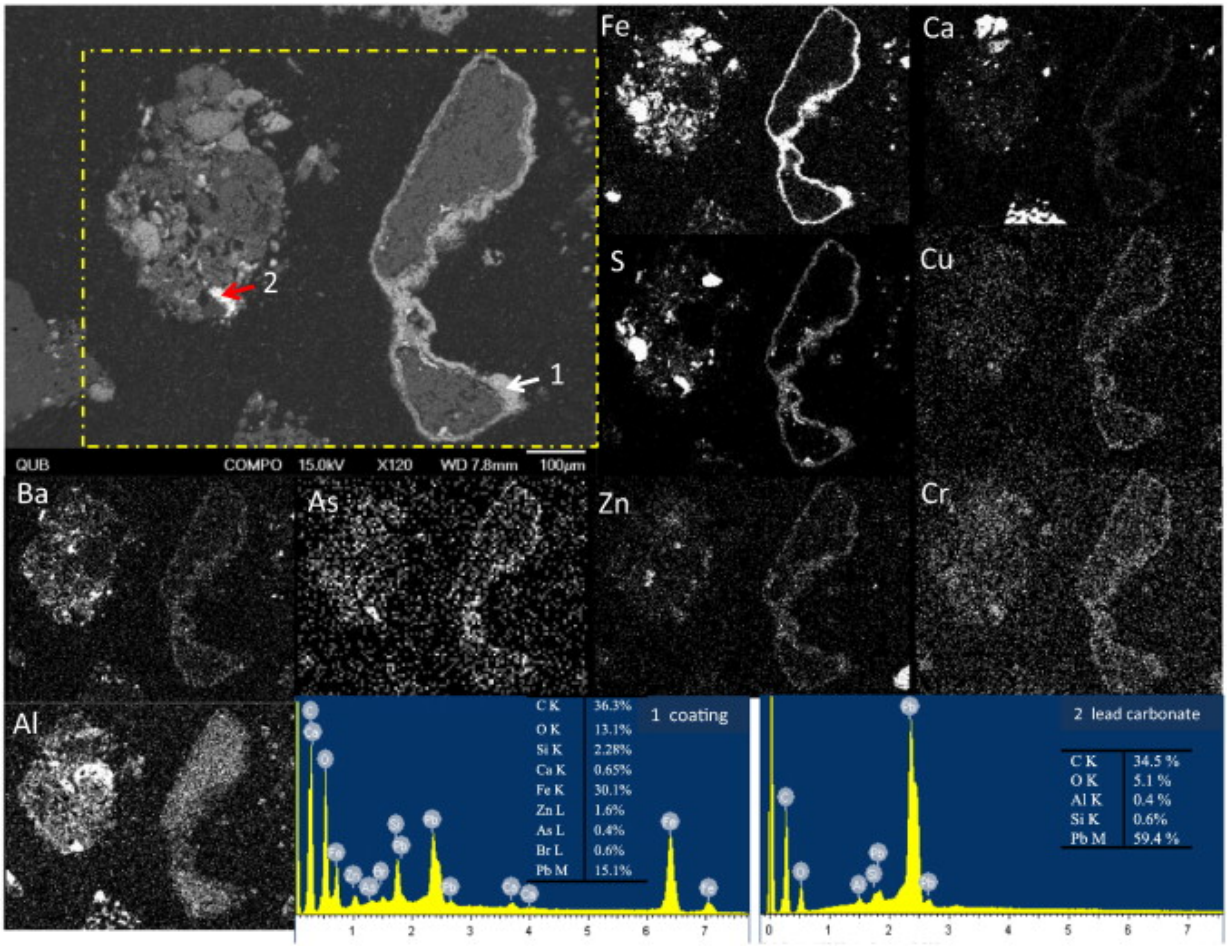
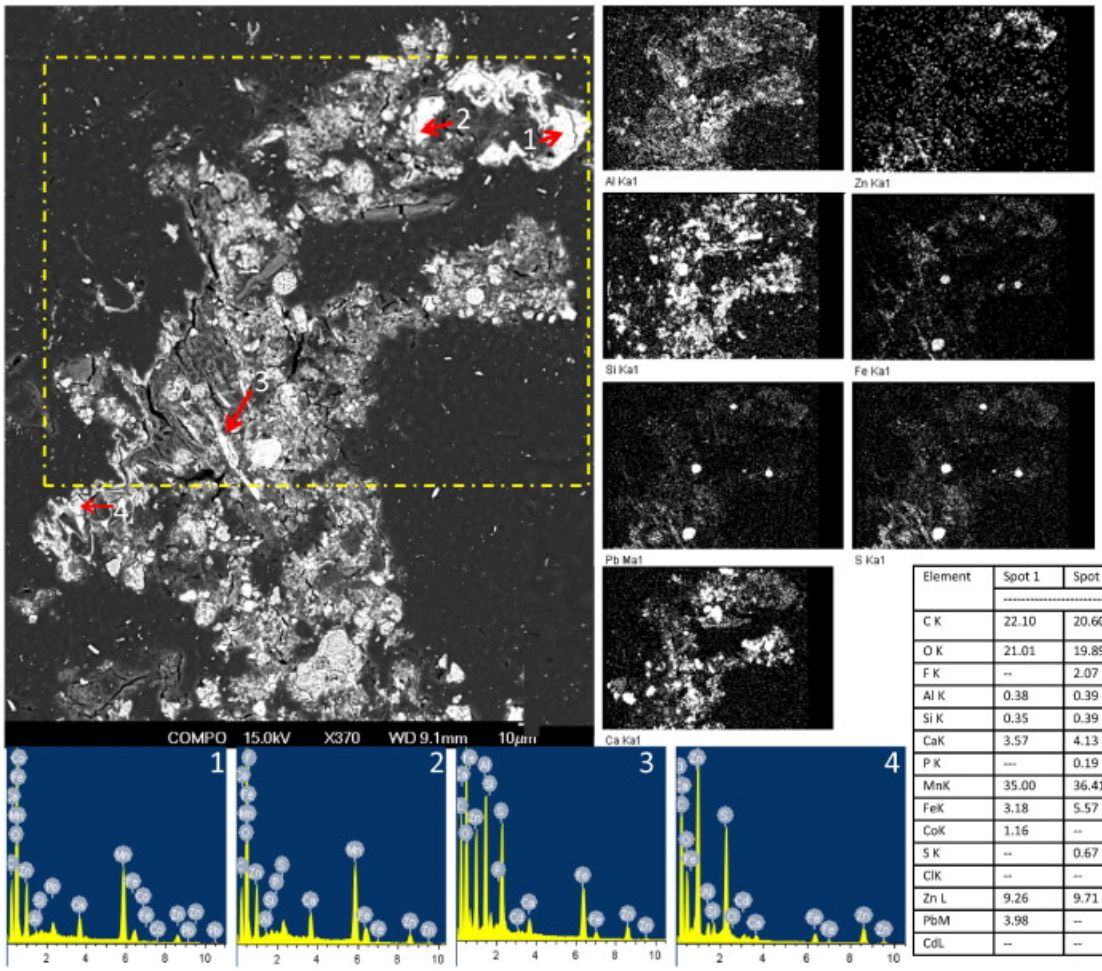


Fig. 6 Photomicrograph, WDS elemental maps and analysis, and SEM-EDS analysis of a silicate mineral and other sediment from the mine spoil area showing a coating (1) rich in metals on a silicate mineral and lead carbonate (2) in other sediment.



Element	Spot 1	Spot 2	Spot 3	Spot 4
	----------%----------			
C K	22.10	20.60	37.37	56.96
O K	21.01	19.89	17.44	10.46
F K	--	2.07	--	--
Al K	0.38	0.39	7.24	0.83
Si K	0.35	0.39	0.92	0.74
CaK	3.57	4.13	1.61	0.67
P K	---	0.19	0.13	--
MnK	35.00	36.41	--	--
FeK	3.18	5.57	18.82	4.09
CoK	1.16	--	--	--
S K	--	0.67	6.37	8.07
ClK	--	--	--	0.38
Zn L	9.26	9.71	9.13	16.06
PbM	3.98	--	--	--
CdL	--	--	0.96	1.74

Fig. 7 Photomicrograph, WDS elemental maps and analysis and SEM-EDS analysis of a fragment of peat encrusted with metals including Zn, Cd, and Pb.

Table 1. Guideline values for metals and anions.

	----------Water---------- mg/L			-----Sediment------ -------mg/kg--------	
	SI No. 294/1989[a]	**WHO Drinking Water Standard**	**SI No. 292/2009[b]**	**CSQS[c]**	**EGS[d]**
pH	5.5-9.0	-	-	-	-
F^-	1	-	0.5	-	-
Cloride	250	-	-	-	-
NO_3^-	50	-	-	-	-
PO_4^{3-}	0.67-0.92	-	-	-	-
SO_4^{2-}	200	-	-	-	-
Ag	-	-	-	1.0	-
Al	-	0.1	-		-
As	0.05	0.01	0.025	7.24	100
Ba	-	0.7	-	-	-
Ca	-	300	-	-	-
Cd[e]	0.005	-	$\leq$0.0002[f]	0.7	-
Cr	0.05	-	0.0034 (CrVI), 0.0047 (CrIII)	52.3	-
Cu	0.05	-	0.005[f]	18.7	-
Fe	-	0.3	-	-	-
Hg[e]	-	-	0.00005	0.2	-
Mg	-	<300	-	-	-
Mn	0.05		-	460	-
Ni[e]	-	0.07	0.02	16	-
Pb[e]	0.05	-	0.0072	30.2	1000
Zn	3.0	-	0.04[f]	120	5000

[a]Statutory Instruments-European Communities Environmental Objectives (Surface Waters) Regulations for the Quality of Surface Water Intended for Abstraction of Drinking Water, 1989
[b]Statutory Instruments-European Communities Environmental Objectives (Surface Waters) Regulations, 2009
[c]Canadian Sediment Quality Guideline value for the Protection of Aquatic Life
[d]EPAI Expert Group for Silvermines Guideline Values for the Protection of Animal Health in Agricultural Soils
[e]Priority Substance in WFD (includes the element and its compounds) (Directive 2008/105/EC environmental quality standards)
[f]AA-EQS for other surface waters under the SI 272/2009

Table 2. Selected metals and organic matter (OM) in surface water and sediment.

ID	Al	Fe	Mn	Ba	Ca	Mg	Al	Fe	Mn	Ba	Ca	Mg	OM
	Surface Water						Sediment						
	mg/L						mg/kg						%
Castletown Stream: Control													
C1	0.41	0.23	0.09	0.0327	213	10.1	-	-	-	-	-	-	
C2	0.57	4.8	0.1	0.0316	216.5	10.4	2165	6755	3408	143	267421	9538	2.78
Upper Barnacullia Stream													
M6	0.0021[1]	0.14	0.04	0.0794	185.1	8.79	-	-	-	-	-	-	-
M5	1.07	0.1	0.1	0.0841	183.3	8.86	3816	38486	18656	4575	106173	10491	53.3
M4	0.0021[1]	0.41	0.15	0.0951	206.6	9.66	6097	14124	2715	2187	179811	10554	21.2
M3	0.0021[1]	1	0.18	0.0946	204.7	9.45	4020	10958	1298	1238	234787	16861	7.41
M2	0.0021[1]	0.81	0.24	0.0983	212.2	9.62	2914	20964	4909	2797	215861	13530	23.5
M1	0.0021[1]	0.57	0.18	0.0979	211.4	9.58	2419	19423	6828	410	224666	7036	-
Lower Barnacullia Stream													
D13	0.0021[1]	0.5	0.2	0.1	219	9.75	8150	35035	7377	2167	125559	7246	-
D12	0.0021[1]	0.25	0.16	0.11	222	9.88	4501	17300	21535	446	269098	14943	23
D11	0.04	7.03	1.15	0.14	234	10.2	5076	27946	8729	4579	181085	9996	-
D10	0.0021[1]	2.08	0.43	0.11	229	9.96	2013	20465	11691	517	233871	7994	-
D9	0.07	0.33	0.36	0.11	211	9.4	-	-	-	-	-	-	-
D8	0.0021[1]	0.13	0.13	0.1	229	9.58	7571	13555	2797	1769	169743	6229	10.1
D7	0.0021[1]	0.06	0.12	0.1	231	9.71	5212	25439	8737	2438	118054	6348	42
D6	0.04	0.08	0.14	0.1	235	9.94	7805	12650	3416	1269	216894	12684	9.71
D5	0.0021[1]	0.06	0.12	0.1	231	9.86	4230	10522	2117	1809	224769	12128	11.1
D4	0.11	0.13	0.05	0.03	217	10.1	7153	10496	2355	601	219872	12620	7.92
D3	0.23	0.17	0.07	0.03	213	10.2	3030	7295	1800	108	232667	8134	2.83
D2	0.0021[1]	0.08	0.03	0.05	215	9.81	4191	12842	2410	1354	188910	13125	-
D1	0.0021[1]	0.23	0.14	0.08	221	9.77	5678	9589	2157	356	232919	8076	-
	Guideline value (SI 294/1989) (Surface Abstraction Standard)						CSQS Values						
	0.1[a]	0.3[a]	0.05	0.7[a]	300[a]	<300[a]			460[b]				

SI No. 294/1989 guideline values. [1]Indicates the value was >LOD. [a]In the absence of a guideline value from SI No. 294/1989, a WHO drinking water quality standard was provided (World Health Organization 2004a, 2004b, 2007). [b]Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (Canadian Council of Ministers of the Environment 1999). Values > guideline values are in red.

Table 3. Linear regression (r^2) values between Fe, Mn, OM and metals/heavy metals in the stream sediments.

	Fe	Mn	Zn	Pb	As	Cd	Cu	Ni	Cr
Fe	--	0.8153	0.9245	0.8656	0.8564	0.855	0.8289	0.7186	--
Mn	0.8153	--	0.8163	0.7111	0.6313	0.6827	0.7284	0.6272	--
OM	0.9421	0.8173	0.834	0.7592	0.7775	0.8421	0.7676	0.8793	0.6897